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XIII. *Additional Experiments on the Muriatic and Oxymuriatic Acids.* By William Henry, M. D. F. R. S. V. P. of the Lit. and Phil. Society, and Physician to the Infirmary, at Manchester.

Read March 19, 1812.

THE experiments, which form the subject of the following pages, are intended as supplementary to a more extensive series, which the Royal Society did me the honour to insert in their Transactions for the year 1800.\* Of the general accuracy of those experiments, I have since had no reason to doubt; and their results, indeed, are coincident with those of subsequent writers of the highest authority in chemistry. My attention has been again drawn to the subject by the important controversy which has lately been carried on between Mr. MURRAY and Mr. JOHN DAVY, respecting the nature of muriatic and oxymuriatic acids;† and I have been induced, by some hints which the discussion has suggested, not only to repeat the principal experiments described in my memoir, but to institute others, with the advantage of a more perfect apparatus than I then possessed, and of greater experience in the management of these delicate processes.

This repetition of my former labours has discovered to me an instance, in which I have failed in drawing the proper conclusion from facts. In two comparative experiments on the electrization of equal quantities of muriatic acid gas, the one

\* Page 188.

† NICHOLSON'S Journal, xxviii. and xxix.

of which was dried by muriate of lime, and the other was in its natural state, I found a difference of not more than one *per cent.* in the hydrogen evolved, relatively to the original bulk of the gas.\* Yet, notwithstanding these results, I have expressed myself inclined to believe that some water is abstracted by that deliquescent salt; and this belief was confirmed, several years afterwards, by the event of an experiment in which muriatic acid gas, dried by muriate of lime, gave only  $\frac{1}{35}$  its bulk of hydrogen,† a proportion much below the usual average. The question, however, was too interesting to be left in any degree of uncertainty; and I have, therefore, made several fresh experiments with the view to its decision. In the course of these I have found, that though differences in the results are produced by causes apparently trivial, some of which I shall afterwards point out, yet that under equal circumstances, precisely the same relative proportion of hydrogen gas is obtained from muriatic acid gas, whether exposed or not to muriate of lime; and that its greatest amount does not exceed  $\frac{1}{16}$  or  $\frac{1}{14}$  the original volume of the acid gas.

In the paper last quoted,‡ I have also described an experiment, in which sensible heat was evolved by bringing muriate of lime into contact with muriatic acid gas; a fact which, if established, would go far to prove the existence of water in that gas. But on repeating the experiment with muriate of lime recently cooled from fusion, and over mercury carefully deprived of all moisture by boiling, I was not able to discover any increase of temperature, though a very sensible air thermometer was inclosed in the vessel containing the gas. The evolution of heat takes place, only when the muriate of lime

\* Page 191.

† Phil. Trans. 1809, page 433.

‡ Page 433 note.

has attracted moisture, either from the atmosphere or the mercury, and is then owing to a condensation of a part of the gas.

Essentially, the changes produced by electrifying muriatic acid over mercury are those which I have stated; viz. a contraction of the volume of the gas, the formation of muriate of mercury (calomel), and the evolution of hydrogen. Recent experiments, also, have confirmed the accuracy of the observation,\* that when a certain effect has been produced by electricity, nothing is gained by continuing the process; for neither is more hydrogen evolved, nor can the contraction of bulk be carried any farther.

I have lately applied, to experiments on muriatic acid, an apparatus which I used advantageously for the analysis of ammonia.† It consists of a spherical glass vessel, into which are hermetically sealed two small tubes containing platina wires, the points of which approach within the striking distance. To the globular part is attached a neck, which may be closed, as occasion requires, either by a glass stopper or by a metal cap and stop-cock. Into a vessel of this kind, I introduced  $4\frac{1}{2}$  cubic inches of muriatic acid gas, and passed through it 3000 discharges from a Leyden jar; at the close of the process, no traces of moisture could be perceived on the inner surface of the vessel, nor could I discover, on opening the stopper, that any change of bulk had taken place. After absorbing the unchanged muriatic acid gas by a small quantity of water, a volume of gas remained, in which there were present 100 measures (each equal to one grain of mercury) of oxymuriatic acid gas, and 140 measures of hydrogen. Two

\* Phil. Trans. 1800. p. 192.

† Ibid. 1809.

causes might, perhaps, contribute to diminish, in some degree, the proportion of the former. It was difficult to exclude from the apparatus, on admitting the muriatic acid gas into it, two or three very minute globules of mercury, which became tarnished during the experiment, exactly as they would have been by oxymuriatic acid; and a small portion of the latter gas was probably also taken up by the water employed to absorb the muriatic acid.

With the intention of giving greater effect to the electricity, I repeated the experiment in a vessel capable of containing not more than 1400 grains of quicksilver (about  $\frac{1}{41}$  of a cubic inch), the neck of which, being only  $\frac{1}{5}$  of an inch in diameter, was better calculated to shew any minute change in the volume of the gas. On removing the stopper, however, no change of volume was apparent. The hydrogen evolved, instead of being more than in the former experiment, equalled in bulk only 20 grains of mercury. The production of oxymuriatic acid was sufficiently evinced by its effect in tarnishing some very small globules of quicksilver, which adhered to the inside of the vessel; but the minuteness of the quantity frustrated an attempt to measure it. From subsequent experiments on similar quantities of gas, confined in the same apparatus, it appeared that the electrization in this last instance had been continued much longer than was necessary; and that an equal effect was produced by  $\frac{1}{8}$  the number of electrical discharges.

In this way of making the experiment, the greatest proportion of hydrogen gas obtainable from muriatic acid amounted only to about  $\frac{1}{70}$ th, while, by electrization over quicksilver,  $\frac{1}{16}$  or  $\frac{1}{14}$  was generally evolved. It was evident, then, that

the mercury had considerable influence over the results; and I found, by experiments with tubes of different diameters, that the larger the surface of the mercury exposed to the gas, the more rapid and complete was the change. Its action was greatly accelerated, also, by causing the electric discharge to strike from the conducting wire, sealed into the tube, to the mercury, which was probably thus raised into vapour; for in some instances, the whole of the inner surface of the glass was coated with sublimed calomel.

The only way, in which the mercury appeared to me likely to be efficient in this case, was by removing the oxymuriatic acid as fast as it was formed; for I have never found any mixture of this gas in the results of experiments on muriatic acid, when carried on over quicksilver. Upon any theory of the constitution of muriatic acid, it may be expected that when, in a mixture of that acid gas with hydrogen and oxymuriatic acid gases, the two latter come to bear a certain proportion to the former, they will be brought within the sphere of mutual agency, and will reproduce muriatic acid. This point appears, from my experiments, to be attained, when the hydrogen and oxymuriatic acid, taken together, have the proportion to the muriatic acid, of about 1 to 35. The amount of the change, therefore, which is capable of being effected on muriatic acid gas, electrified without the contact of mercury, is limited by the reaction of the evolved hydrogen and oxymuriatic acid gases on each other, whenever they compose a certain proportion of the mixture. This proportion being attained, we only, by continuing the electrization, work in a circle.

It may now be inquired, what is the limitation to the action of electricity on muriatic acid gas which is confined over mer-

cury? In this case, it was suggested to me by Mr. DALTON, who favoured me with his presence at most of the experiments, that the evolved hydrogen might possibly in some way prevent the effect from being carried beyond a certain amount. Availing myself of this hint, I mixed 30 measures of hydrogen gas with 400 of muriatic acid gas in its ordinary state, and passed 900 discharges through the mixture. It soon became evident that the addition of the hydrogen had produced an important difference in the results of the experiment; for the surface of the mercury, over which the gas rested, was untarnished after some hundred explosions, and was scarcely changed at the close of the process. When the residuary gas, the volume of which remained unaltered, was analyzed, it was found to contain the same quantity of muriatic gas as at the outset, and neither more nor less hydrogen. To explain the event of this modification of the experiment, on the old theory, we may suppose that by the action of electricity a particle of water is decomposed, and that the atom of oxygen, forcibly repelled from that of hydrogen with which it was associated, finds another atom of hydrogen uninfluenced by the electric fluid, and within the sphere of its attraction. With this it unites, and recomposes water. On the theory of Sir H. DAVY, the same series of decompositions and recombinations may be assumed to take place between the oxymuriatic acid and hydrogen.\*

\* I am aware that there is an apparent inconsistency in supposing changes of precisely an opposite kind to be effected by the same means. But instances are not wanting, in which the very same elements are brought into combination by electric discharges, and are again disunited by the same agency. As examples, it may be sufficient at present to state, that nitrous acid and nitrous gas are generated by the action of the electric spark on mixtures of oxygen and nitrogen gases; and that, by

It still, however, remains to be determined, what is the source of the hydrogen gas, which, in a limited proportion, is always evolved by the electrization of muriatic acid? Does it result from the decomposition of water, existing as an element of the gas; or from the disunion of the oxymuriatic acid and hydrogen, which, according to Sir H. DAVY's view, compose muriatic acid? The limitation to its amount, which, it formerly appeared to me,\* could only be accounted for by the complete destruction of the water contained in the gas, may now be equally well explained, on the principle which I have just pointed out. The fact, also, that no appreciable change of bulk is produced by the electrization of the muriatic acid, when the presence of mercury is excluded, is perhaps favourable to the new theory. For since equal measures of hydrogen and oxymuriatic acids afford muriatic acid without any condensation of volume, no alteration of bulk should result from the disunion of those elements; and the products should be equal measures of the same gases. The proportions, which I obtained (100 to 140) did not, it must be acknowledged, exactly correspond with the theory; but the difference was not greater, than might naturally be expected from the circumstances of the experiment. That equal measures of hydrogen and oxymuriatic acid are really evolved, appears to me to be proved by the agreement, which I have in several experiments remarked, between the hydrogen gas obtained,

the same power, they are again resolved into their elements. If this were the proper place, it might, I think, be rendered probable by several arguments, that electricity, when thus applied, acts rather by mechanical collision, than by inducing a change in the electrical states of the elements of bodies.

\* Phil. Trans. 1800, p. 200.



and the contraction of volume in muriatic acid electrified over mercury. Now the latter effect of the process can be explained on no other principle than the absorption of oxymuriatic acid by the quicksilver.

When muriatic acid and oxygen gases are electrified together over mercury, a gradual diminution ensues in their bulk,\* and the mercury becomes tarnished, precisely as by the contact of oxymuriatic acid. I have lately examined the agency of this process on a considerable quantity of the two gases confined in a vessel, into which they were admitted after exhausting it by the air-pump. The phenomena, which in this way of making the experiment are extremely decisive and interesting, are the production of water and of oxymuriatic acid. The former, combining with a portion of the undecomposed muriatic acid, is deposited in drops upon the inner surface of the vessel, in the state of liquid muriatic acid. When the stop-cock, which confine the gases, is opened under mercury, a quantity of that metal rushes in, and has its surface instantly tarnished. Besides this test of the production of oxymuriatic acid, its presence is rendered unequivocal (after absorbing the undecomposed muriatic acid by a few drops of water), both by its smell, and by its effect in discharging the colour of litmus paper.†

These results, it will be found, may be reconciled with

\* Phil. Trans. 1800, p. 193.

† Those who wish to repeat this experiment need not be deterred by the apprehension of the labour attending it; for 3 or 400 discharges, from a Leyden jar of moderate size, are sufficient to occasion a distinct precipitation of moisture. When a mixture of oxygen and muriatic acid gases is even suffered to stand over mercury, a gradual contraction of volume takes place; the muriatic acid, if in proper proportion, entirely disappears; and calomel is deposited upon the surface of the glass vessel; but, in this case, there is no visible production of moisture.

either theory. According to the one which has been commonly received, the oxygen unites with the real acid of muriatic gas, which becoming oxymuriatic acid, *deposits* water. On Sir H. DAVY's view, the oxygen unites with the hydrogen of the muriatic acid, and *composes* water, while the oxymuriatic acid is merely an educt. I am not aware of any refinement of the process, by which the value of these two explanations can be compared. Something, however, would be gained by a precise determination of the proportions, in which the two gases saturate each other. For since, on Sir H. DAVY's theory, muriatic acid contains half its volume of hydrogen gas, two measures of which are known to be saturated by one of oxygen, it follows that muriatic acid gas should be changed into oxymuriatic by one-fourth of its bulk of oxygen. According to GAY LUSSAC and THENARD,\* three measures of muriatic acid should condense one of oxygen (or only one-third their bulk), and should form two measures of oxymuriatic acid. Hitherto, I have not been able to satisfy myself respecting the true proportions of oxygen and muriatic acid gases, that are capable of being united by electricity; for though I have made several experiments with this view, they have not agreed in yielding similar results. The condensation of a part of the undecomposed acid by the water, which is formed during the process, will, probably, indeed, always be an impediment to our learning these proportions exactly. The fact is chiefly of value, as it affords an example of the production of oxymuriatic acid under the simplest possible circumstances; and as it shews unequivocally that, under such circumstances, the visible appearance of moisture is a part of the phenomena.

\* Mémoires d'Arcueil, ii. 217.